

## ELECTROCHEMICAL BEHAVIOUR OF BINARY PALLADIUM ALLOYS

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Palladium forms binary alloys with nickel and platinum without miscibility gap. All alloys represent the same lattice symmetry, i.e. face centred cubic structure [1,2]. It is known that the absorption of hydrogen in these alloys is lower than in pure Pd. The aim of this communication is to present the results of the investigation of the electrochemical absorption of hydrogen in binary Pd-Ni and Pd-Pt electrodes with limited volume (LVE) [3].

The alloys were electrodeposited potentiostatically on a gold matrix (Au wire or Au covered AT quartz crystal) from baths containing salts of the appropriate metals. Bulk compositions of the alloys were determined using EDAX method, while surface compositions of the alloys were estimated from the electrochemical data. The amount of adsorbed and absorbed hydrogen was calculated from the oxidation current peaks [3,4]. Measurements were performed in basic (Pd-Ni and Pd-Pt alloys) and acidic (Pd-Pt alloys) solutions.

In Pd-Ni alloys, hydrogen absorption has been studied using electrochemical quartz crystal microbalance (EQCMB). Hydrogen absorption has been accompanied by an increase of the frequency ( $\Delta f$ ), i.e. an increase in mass of the electrode, according to the Sauerbrey equation. The opposite trend is observed during the desorption process. However, these mass changes are surprisingly high in comparison with the masses calculated from charges ( $q$ ) obtained from the electrochemical data. Similarly to the case of pure palladium [4], these results show that the microbalance response ( $\Delta f/q$ ), in the whole potential range studied, is strongly affected by the stresses generated inside the metal lattice during the hydrogen absorption/desorption process and depends on the amount of absorbed hydrogen for both  $\alpha$  and  $\beta$  phases of absorbed hydrogen. The effect of stress inside the alloy lattice observed for the Pd-Ni alloy might be linked to the relative changes of the alloy lattice constant due to the absorption of gaseous hydrogen [1].

The stress effect was investigated for the Pd-Ni alloy in the concentration range of 8-35 atomic % of Ni. The slope changes on the  $\Delta f/q$ -%Ni plots occur in the concentration range of 20-30 %at. Ni, i.e. in the same composition range as the changes of electronic and magnetic properties of the alloy [5]. More importantly, these slope changes correspond to an abrupt decrease of the sorption capacity of the Pd-Ni alloy [3].

Further EQCMB investigation of Pd-Ni alloys provided additional information about electrochemical behaviour of this system. Mass response obtained during  $\text{Ni(OH)}_2$  oxidation strongly

suggests that this process is accompanied by the alkali cation incorporation into the alloy lattice, an effect well known for pure nickel electrode [6]. The shape of EQCMB response also suggests that one form of nickel hydroxide,  $\alpha\text{-Ni(OH)}_2$  is stabilised on Pd-Ni alloys in basic solutions.

In case Pd-Pt alloys not only bulk but also surface composition of the alloy could be estimated and hydrogen sorption could be related to both composition values. Even if the surface concentration of platinum is as high as 80-90 atomic %, but bulk Pt content does not exceed 25 at.%, hydrogen absorption still occurs. On the other hand at bulk platinum content as high as 80-90 at.%, no hydrogen absorption is observed. It can be concluded, therefore, that hydrogen absorption in the Pd-Pt alloy is governed, almost exclusively, by the composition of the bulk of the alloy.

From the data obtained for Pd-Ni and Pd-Pt alloys some conclusions about the kinetics of hydrogen absorption process in these alloys has been drawn. The generation of new form of adsorbed hydrogen, OPD (overpotentially deposited) hydrogen is suggested at potentials cathodic to the reversible hydrogen potential. This form probably participates in the overall absorption reaction and is responsible for the changes of the kinetics of this process at potentials where OPD hydrogen is generated, both in basic and acidic solution.

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